Role of self-irradiation defects on the ageing of 239PuCoGa5

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Role of self-irradiation defects on the ageing of ^{239}PuCoGa$_5$

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Abstract. - Low temperature accumulation and annealing experiments, in conjunction with electrical resitivity and critical current density measurements, are used to study the ageing of the actinide superconductor PuCoGa$_5$. These measurements reveal that 2-nm sized non-superconducting point-like regions are the main damage formed during room temperature ageing; smaller point like defects are irrelevant to transport properties. Defect sizes and densities deduced from experiment agree with Transmission Electron Microscopy observations.

Introduction. – The discovery of superconductivity in PuCoGa$_5$ [1], with characteristics intermediate between heavy-fermion compounds and HTSC, has raised a great deal of interest because of its possible unconventional nature. The PuCoGa$_5$ superconductor is unique in that defects are spontaneously produced by the α-decay of the Pu atoms. The effect of this "self-irradiation" induced ageing on the normal-state and superconducting properties of PuCoGa$_5$ are quite remarkable and tentative explanations in terms of unconventional superconductivity have been put forward [2]. The defect densities attainable by self-irradiation of bulk samples are high compared to what may be obtained in heavy-fermion compounds by more conventional irradiation techniques. Among these are exposure at low temperature to high energy electrons, yielding homogeneously distributed point defects [3-5], or irradiation with swift heavy ions resulting in the creation of amorphous columnar tracks [6]. Contrary to the latter techniques, detailed knowledge of self-irradiation damage is not available. It is the aim of this paper to identify the defect type most relevant for the change of superconductivity parameters during ageing of PuCoGa$_5$. For this, we combine transport measurements in the normal and superconducting state with low temperature accumulation and annealing experiments. We find that non-superconducting point defects of dimension ~ 2 nm quantitatively account for observed changes of the critical current. The deduced defect sizes and densities are in agreement with defects observed in Transmission Electron Microscopy (TEM).

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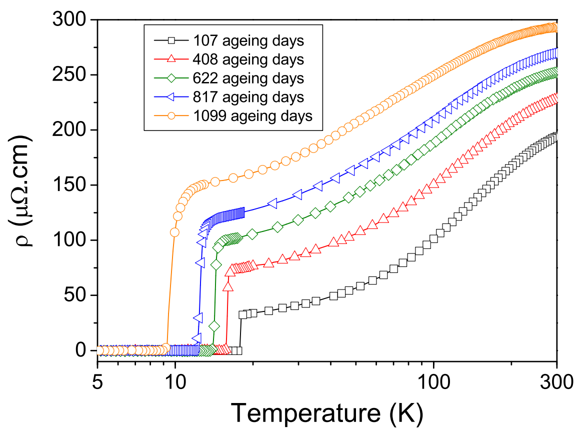

Fig. 1: Variation of the resistivity versus temperature curve of the ^{239}PuCoGa$_5$ polycrystal.

Experimental. – Polycristalline samples were synthesized by arc melting and single crystals were grown in Ga flux. The precise operational mode of the synthesis is described in [7]. DC-magnetisation measurements have been performed on a Quantum Design SQUID magnetometer from 2 to 300 K in magnetic fields up to 7 T. Electrical resistivity was measured by a Quantum Design PPMS-9 over the range 1.8 - 300 K in magnetic fields up to 9 T. All measurements are performed on encapsulated samples to avoid radioactive contamination. The sample is placed in a German silver tube ($Cu_{62}Ni_{18}Zn_{20}$ alloy) for magnetisation measurements or in a copper sampleholder sealed by Stycast at its extremities for resistivity measurements.

Given the energy of the ^{235}U recoil atom ($\sim$ 90 keV), three different types of defects can be generated by self-irradiation: (i) isolated point defects (or Frenkel pairs), (ii) dislocation loops and (iii) point defect clusters formed in the wake of the recoil atom. The two latter result from the agglomeration of isolated point defects. Isolated Frenkel pairs and dislocations loops are expected to act as weak pinning centers for flux vortices in the superconducting mixed state, *i.e.* only the defect density fluctuation leads to a net pinning force. On the other hand, point defect clusters are thought to act as strong point-like flux pinning centres. In that case, the pinning force from each defect cluster should be directly summed to obtain the total pinning force [8]. The sustainable ("critical") current density in the two cases displays a very different field dependence, which should allow an easy identification of the most relevant defect type [8].

In order to determine the influence of isolated point defects on the ageing of ^{239}PuCoGa$_5$, we have first performed accumulation experiments at 4.2 K on a ^{239}PuCoGa$_5$ polycrystal having already undergone 460 days' ageing at room temperature. At 4.2 K, the defect mobility and recombination rate are much reduced, so that created point defects will remain isolated. The following procedure was adopted for the accumulation experiments (inspired from the work of [9] on self-irradiated δ-Pu). First, a resistivity measurement is performed by cooling the sample to 4.2 K, followed by data acquisition upon warming. This constitutes the resistivity curve before accumulation. Second, the sample is cooled again and maintained at 4.2 K during the time of accumulation. No measurement is done at this stage: the compound is in the superconducting state and $R = 0$. After a certain time, the effect of the accumulation is observed by measuring the resistivity on warming the sample to 300 K (resistivity curve after accumulation). Finally, to determine whether a partial annealing of the added point defects occurs at 300 K, another resistivity measurement is performed immediately afterwards (room temperature recovery curve).

The sustainable current density J was obtained from the measurement of the non-equilibrium magnetic moment and application of the Bean critical state model [10], using the formula for a rectangular solid of lateral dimensions $a < b$/[cm] with a magnetic field applied perpendicularly to one of its faces:

$$J/[A.cm^{-2}] = \frac{20\mu}{m}\frac{M^+ - M^-}{a\left(1 - \frac{a}{3b}\right)} \quad (1)$$

Here M^+ and M^- denote the magnetisation measured on the increasing and decreasing magnetic field branch respectively, μ/[g.cm^{-3}] is the volume mass and m/[g] is the sample mass. Note that the sustainable current decreases with time due to the thermally activated motion of vortices (flux-creep) [11]. Flux creep experiments were carried out

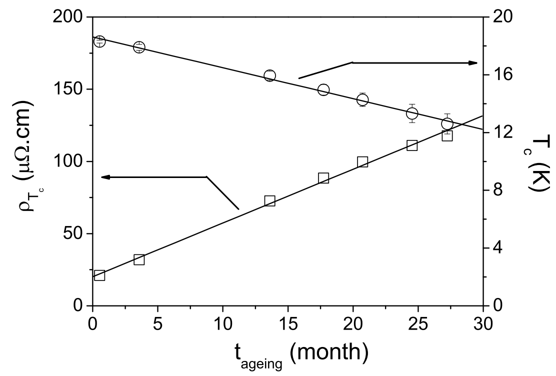

Fig. 2: Evolution of ρ_{Tc} (left axis) and T$_c$ (right axis) versus ageing time of the ^{239}PuCoGa$_5$ polycrystal.

by measuring the temporal evolution of the magnetisation at a fixed temperature below T_c and for a fixed magnetic field, chosen to lie above full flux penetration field H_p, to ensure that the sample is entirely permeated by vortices.

Microstructure observations were performed on a sample of ^{239}PuCoGa$_5$ aged one year at room temperature using a Hitachi H700 200 kV Transmission Electron Microscope (TEM), modified for the examination of radioactive compounds and equipped with an energy dispersive X-ray spectroscopy analyzer (EDX). The sample has been ground in ethanol in a glove-box and pieces with appropriate thickness (thin enough to be electron transparent) were selected.

Results. – Fig. 1 shows the effect of room-temperature ageing on the resistivity of a ^{239}PuCoGa$_5$ polycrystal. Typically, the resistivity increases linearly with ageing time, while the critical temperature T_c decreases (Fig. 2). These experiments are compared to four accumulation experiments performed at 4.2 K, on another ^{239}PuCoGa$_5$ polycrystal (Fig. 3 & 4). For accumulation times of 84.2 and 83.9 hours, no effect could be observed. However, following accumulations over 400 and 800 hours respectively, an overall increase of the resistivity, and a decrease in T_c, both comparable to the effect of room-temperature ageing for *several weeks*, are observed.

After warming the sample at 300 K, the resistivity decreases but remains higher than its value before accumulation. The same trend is observed for T_c: its value is enhanced after annealing at 300 K but remains lower than it was before the experiment. This indicates a partial annealing, at 300 K, of the defects created at low temperature. In order to quantify these effects, we report the evolution of ρ_{Tc}, the value of resistivity taken at the onset of the superconducting transition, versus time (Fig. 5 & 6). For ageing at 300 K, a linear evolution $\rho_{Tc}(t_{ageing})$ is observed, in agreement with the contribution of self-irradiation defects to the resistivity expected from the radioactive decay law [12]. This contribution is proportional to (1 - e$^{-\beta t}$)

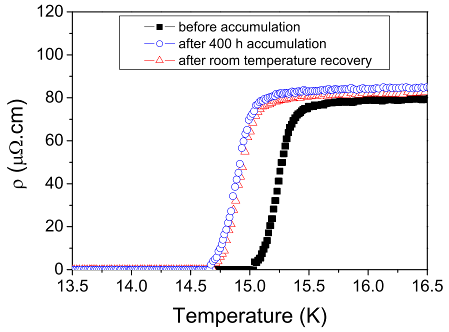

Fig. 3: Resistivity curves resulting from 400 hours low temperature accumulation experiment of aged $^{239}PuCoGa_5$ polycrystal. ■: before accumulation; ○: after accumulation; △: after annealing at 300 K.

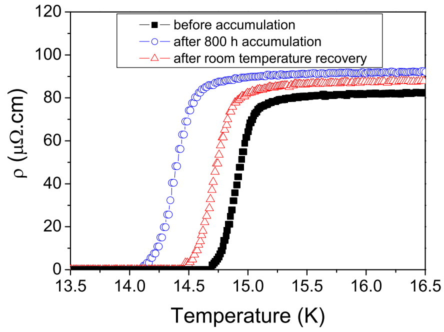

Fig. 4: Resistivity curves resulting from 800 hours low temperature accumulation experiment of aged $^{239}PuCoGa_5$ polycrystal. ■: before accumulation; ○: after accumulation; △: after annealing at 300 K.

where β is a constant depending on the intrinsic properties of the studied compound. Considering the time of our study compared to the half-life of ^{239}Pu ($T_{1/2}$ ~ 24,000 *years*), the resistivity contribution from self-irradiation increases linearly with time. The Matthiessen law [13] is respected and no saturation is observed, as one could expect due to self-irradiation of Pu atoms [14].

The ρ_{Tc} data measured after low-temperature accumulations of 400 and 800 hours experiments show a clear deviation from the linear evolution. Nevertheless, after room temperature recovery, the values of ρ_{Tc} coincide exactly with the 300 K ageing data, indicating that *all* point defects accumulated at low temperature are totally annealed at 300 K. We conclude that isolated point defects have little or no influence on the ageing effects observed at room temperature, and can be disregarded in further discussions. To further characterize the defect structure, we turn to the hysteretic magnetisation of the $^{239}PuCoGa_5$ polycrystal. Fig. 7 shows the sustainable current density at T = 5 K extracted using Eq (1). The overall shape of the $J(H)$ curve, with constant current density at low fields, and a rapidly decreasing current density for fields higher than some characteristic value B^*, is characteristic of a type-II superconductor containing strong point-like pins [8]. It is notably different from the *field-independent* behaviour of the critical current in the isostructural $CeCoIn_5$ compound, in which pinning is thought to be due to small dislocation loops [15]. Thus, no dominant effect of small dislocation loops can be identified in the $PuCoGa_5$ material.

In order to estimate the density of self-irradiation induced defects, the current density versus magnetic field data are fit by a phenomenological exponential law for strong individual pinning of flux lines by strong point-like pins [8],

$$J_c = J_c(0)\left[1 - \exp\left(-\frac{B^*}{\mu_0 H}\right)\right] \qquad (2)$$

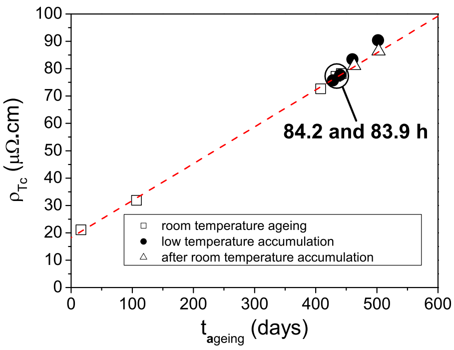

Fig. 5: Evolution of ρ_{Tc} versus ageing time of the $^{239}PuCoGa_5$ polycrystal. □ : after ageing at 300 K, *i.e.* without any low temperature accumulation; •: after accumulation at low temperature; △: after room temperature recovery.

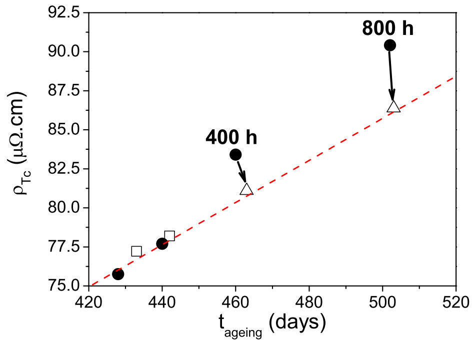

Fig. 6: Enhancement of Fig. 5 for accumulations of 400 and 800 h.

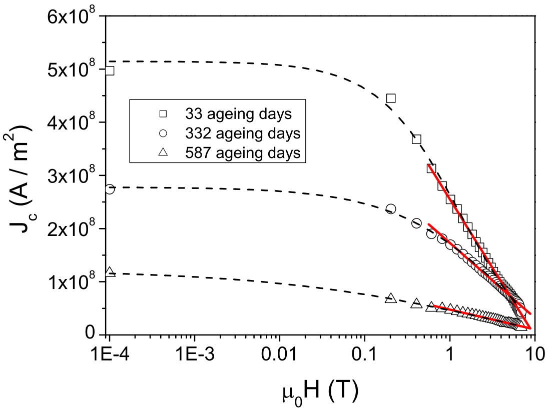

Fig. 7: Sustainable current densities extracted from magnetisation hysteresis experiments on a ^{239}PuCoGa$_5$ polycrystal at T = 5 K. Drawn lines denote fits to Eq. 2. Dashed lines are guides for the eye.

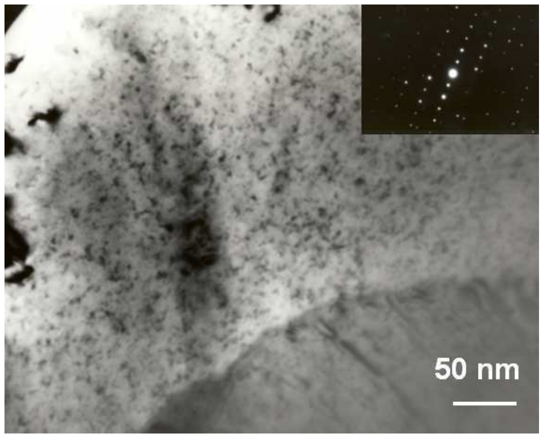

Fig. 8: Characteristic TEM micrograph of ^{239}PuCoGa$_5$ single crystal, performed in bright field after one year of ageing. Black dots represent $\sim$ 2 nm-sized defects, homogeneously distributed throughout the sample. The inset shows the diffraction pattern recorded in the same zone, indicating a persistent tetragonal crystalline nature.

Such a law expresses the probability that the vortex line, threading an area $a_0^2 \sim \phi_0/B$, is trapped by at least one defect, assuming that the latter are distributed according to a Poisson law, with a mean separation between defects $\langle r \rangle \equiv n_d^{-1/3} \equiv (\phi_0/B^*)$. Here $\phi_0 = h/2e$ is the flux quantum, $B = \mu_0 H$, and $\mu_0 = 4\pi \times 10^{-7}$ Hm^{-1}). The characteristic field $B^* \approx \pi\phi_0 n_d U_P/\varepsilon_0$ is determined by the balance of pinning energy gain U_P and increasing inter-vortex repulsion $\varepsilon_0 \left(\langle r \rangle / a_0\right)^2$ when a flux line is displaced onto a defect. The characteristic vortex energy is $\varepsilon_0 = \phi_0^2/4\pi\mu_0\lambda^2$ with λ the penetration depth. The pinning energy gain due to an insulating defect is given by the ratio of its cross-section and that of the vortex core, $U_P = \varepsilon_0 D_i \left(D/2\xi\right)^2$, with $\xi \approx 2$ nm [1] and with $D_i \approx D \approx 2.3$ nm the dimensions of typical defects observed in Transmission Electron Microscopy (TEM, see Fig. 8). We can then relate

$$B^* \approx \pi\phi_0 n_d D_i \left(\frac{D}{\xi}\right)^2 \approx 2\pi^2 B_{c2} f_d. \tag{3}$$

to the volume fraction f_d of the material rendered non-superconducting by the self-irradiation ($B_{c2} = \phi_0/2\pi\xi^2$ is the upper critical field). Collecting temperature dependences of λ and ξ, the defect density $n_d \sim 5.2\times10^{22} B^*(1+\vartheta)/(1-\vartheta)$, with $\vartheta \equiv T/T_c$, can be estimated from fits of the $J(H)$ data to Eq. (2). The explicit inclusion of the dependence on *reduced* temperature ϑ corrects for the decrease of the critical temperature with ageing. Table I regroups defect densities deduced in this manner, as function of sample age. These values are in good agreement with defect densities observed using TEM (Fig. 8), but their values are substantially lower than the absolute number of ^{239}Pu decays at the sample age t_{ageing}. We surmise that the discrepancy is due to the partial annealing of defects

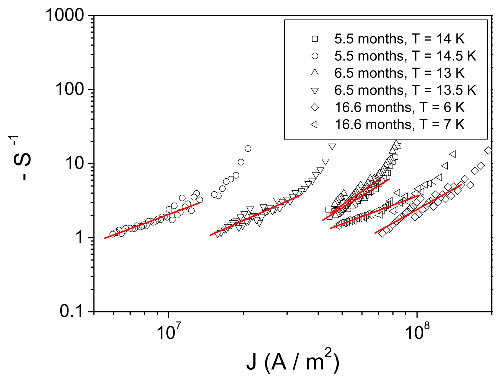

Fig. 9: Inverse relaxation rate S versus current density J of ^{239}PuCoGa$_5$ single crystal. Drawn line is a fit to Eq. 5.

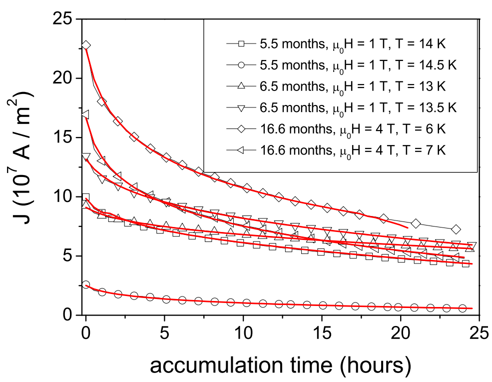

Fig. 10: Screening current density J of ^{239}PuCoGa$_5$ single crystal versus time . Drawn line is a fit to Eq. 4.

Table 1: Parameters deduced from the fits of $J(H)$ at $T = 5$ K for a $^{239}PuCoGa_5$ polycrystal by an exponential law. N is the number of disintegrated Pu atoms. The mean distance between defects is denoted $d_d \equiv n_d^{-1/3}$. f_{damage} is the damaged fraction of the sample, calculated by $n_d \times D_i \times D^2$.

t_{ageing} (days)	$N(t_{ageing})$ (m^{-3})	T_c (K)	(1-ϑ)/(1+ϑ)	$B^*(T)$	n_d (m^{-3})	d_d (nm)	f_d (%)
33	4×10^{23}	18	0.57	1.2	1.1×10^{23}	21	0.14
332	4×10^{24}	15.9	0.52	2.5	2.5×10^{23}	16	0.31
587	7×10^{24}	13.2	0.45	2.8	3.2×10^{23}	15	0.39

Table 2: Data and physical quantities deduced from flux creep fits of $^{239}PuCoGa_5$ single crystal.

t_{ageing} (month)	T_c (K)	B (T)	$T(K)$	α	J_0 (Am^{-2})	k_BT/U_0	τ (h)	U_0/k_B (K)
5.5	16.6	1	14	2.15	4×10^{11}	0.553	10.1	25.3
			14.5	1.07	7×10^{6}	0.877	20.9	16.5
6.5	16.4	1	13	2.68	9×10^{10}	0.623	18	20.9
			13.5	1.77	1×10^{8}	0.371	5.2	36.4
16.6	14.4	4	6	1.85	1×10^{8}	0.864	13.9	6.9
			7	1.07	4×10^{7}	0.856	32.6	8.2

at room temperature issued from the α-decays. However, the good agreement between defect densities $\sim 10^{23}$ m^{-3} observed in TEM and deduced from critical current measurements leads to the conclusion that 2 nm-sized point like insulating regions are the main damage caused by self-irradiation. The damaged volume is substantially smaller than that recently deduced from EXAFS studies [16].

The relevance of nm-size point-like pinning centers is comforted by flux-creep experiments performed on a single crystal of $^{239}PuCoGa_5$. In the case of strong pinning by point defects, the creep-induced electric field is activated, $E \sim \exp\left(-U(J)/k_BT\right)$, with an activation barrier of the form $U(J) = U_0\left[1 - (J/J_0)^\alpha\right]$ [17, 18]. Combining this with Maxwell's equations, the temporal decay of the screening current follows

$$J(t) = J_0\left[1 - \frac{k_BT}{U_0}\ln\left(\frac{t_0+t}{\tau}\right)\right]^{1/\alpha} \tag{4}$$

with U_0 the potential barrier extrapolated to zero current, J_0 the initial current density, and t_0 a measure of the transient behaviour at the start of the experiment. The characteristic time $\tau = \mu_0 a^2 U_0/\rho_f k_B T$ depends on the flux-flow resistivity ρ_f and the typical lateral sample dimension a. The conformity of the experimental results to Eq. (4) is tested by plotting the inverse relaxation rate,

$$-S^{-1} = -\left[\frac{\partial \ln J}{\partial \ln t}\right]^{-1} = \frac{\alpha U_0}{k_BT}\left(1+\frac{t_0}{t}\right)\left(\frac{J}{J_0}\right)^\alpha,$$
$$-S^{-1} \approx \frac{\alpha U_0}{k_BT}\left(\frac{J}{J_0}\right)^\alpha (t \gg t_0)\,, \tag{5}$$

in Fig. 9 & 10. From the graph, we obtain the power $\alpha \approx 2$, as well as $U_0/k_BTJ_0^\alpha$. A fit to the original $J(t)$ data gives J_0, t_0, and τ. The results and parameters of all the experiments performed are given in Table II. Again, the decrease of the critical current with ageing, due to the decrease of T_c and the condensation energy outweighs the increase of J_c due to the increasing number of defects.

In summary, accumulation and annealing experiments, in correlation with resistivity and critical current measurements, lead to the conclusion that the relevant self-irradiation damage in $PuCoGa_5$ consists of nm-sized point defect clusters (non-superconducting regions). The nature of these defects should be taken into account in future discussion of scattering rates and pair-breaking effects in this material.

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